

Combination of carbon nanotubes and two-photon absorbers for broadband optical limiting

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Abstract

New systems are required for optical limiting against broadband laser pulses. We demonstrate that the association of non-linear scattering from single-wall carbon nanotubes (SWNT) and multiphoton absorption (MPA) from organic chromophores is a promising approach to extend performances of optical limiters over broad spectral and temporal ranges. Such composites display high linear transmission and good neutral colorimetry and are particularly efficient in the nanosecond regime due to cumulative effects.

1 Introduction

Active eye and sensor protection against high power laser is an operational need of growing importance due to the democratization of frequency-agile pulsed lasers. An ideal optical limiter should fulfill high-level specifications, like broadband optical limiting efficiency over the whole visible spectrum, and broadband temporal efficiency from sub-nanosecond pulses to continuous regime. Furthermore, it should also preserve the quality of observation/detection at low fluences and should therefore display high linear optical

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transmittance and neutral colorimetry. Extensive researchs were conducted over the past fifteen years and led to the emergence of three main classes of nonlinear optical materials : reverse saturable absorbers [1], multiphoton absorbers [2] and nonlinear scattering systems [3,4]. However, none of these systems, *taken individually*, is able to fully fulfill the specifications listed above. Some attempts were performed with combinations of nonlinear optical materials in cascaded geometries : multi-plate or tandem cells [6], use of two intermediate focal planes of a sighting system [7].

In this letter, we propose a new approach for the design of composite optical limiters, in which two complementary nonlinear optical materials are mixed together in the same cell. Indeed, we studied mixtures of single wall carbon nanotubes (SWNT) suspensions, which were recently shown to be effective optical limiters [4], and multiphoton absorbers (MPA) solutions. Nonlinear scattering is the main limiting phenomenon for SWNT suspensions, due to the growth of solvent vapor bubbles at low fluences and long pulses, and to the growth of carbon bubbles from nanotube sublimation at high fluences and short pulses [5]. Optical limiting is effective for relatively long pulses, typically from the nanosecond to the microsecond regimes. As far as MPA solutions are concerned, their strong multiphoton absorption cross-sections are responsible of limitation, which is effective for shorter pulses (subpicosecond to a few nanosecond). The materials and the experimental aspects of the work are presented in section 2. The association of the non linear scattering properties of SWNT and the multiphoton absorption properties of MPA is investigated in the nanosecond regime in section 3. We finally discuss the expected optical limiting performances of such composites from picosecond to microsecond regimes in section 4.

2 Materials and Experimental

SWNT were produced by the electric arc process and were purchased from Nanoledge[®] and MER[®]. These samples were extensively characterised using scanning and transmission electron microscopy, X-Ray diffraction, Raman and optical spectroscopy [8]. The mean diameter of the nanotubes is approximately of 1.4 nm. Suspensions of as-produced, raw samples (from Nanoledge[®]), hereafter referred as NT-Raw, were prepared in chloroform [4]. By contrast, purified nanotubes (from MER[®]) could not be suspended in chloroform. These purified nanotubes were made soluble in chloroform by grafting long alkyl chains on their surface [9]. Indeed, acidic treatment (H_2SO_4 / HNO_3 (3/1)) of the nanotubes leads to the formation of carboxylic groups on the nanotube surface [10]. Activation of these groups with thionyl chloride followed by coupling with octadecylamine yields grafted nanotubes which are fully soluble in

chloroform [11]. The linear transmittance spectra of suspensions of raw and functionalised samples (hereafter designated as NT-Graft) are almost undistinguishable (not shown). The optical limiting properties of as-produced nanotubes and grafted purified nanotubes suspensions in chloroform are similar, whatever the pulse duration.

2,2'-([1,1'-biphenyl]-4,4'-diyl-di-2,1-ethenediyl)-bis-benzenesulfonic acid disodium salt, most usually named *Stilbene-3* [12], is a commercially available dye which was used as reference compound for multi-photon absorption. Solubility of stilbene-3 is high (300 g/l) in DMSO and moderate (20 g/l) in water but stilbene-3 is insoluble in chloroform. In order to achieve solubility of stilbene-3 in chloroform, sodium counter-ions were exchanged with quaternary dimethyldioctadecyl ammonium groups. The presence of ammoniums bearing long alkyl chains on the dye allowed modified stilbene-3 to be soluble in CHCl_3 (>200 g/l).

Linear optical transmission of SWNT suspensions were adjusted to 70 % at 532 nm in 2 mm thick cells. For such transmittances, the nanotube concentration was around 10 mg/l. The MPA concentration in the reference sample and in the composites was 50 g/l. Nonlinear optical transmittance measurements were performed using different laser sources and test beds : (i) a RSG-19 experimental set-up in a F/5 focusing geometry with a 1.5 mrad collecting aperture [13], using a frequency-doubled Nd:YAG laser emitting 7 ns pulses at 532 nm (ii) an optical parametric oscillator (OPO) with a pulse duration of 3 ns at 532 nm, in a F/30 focusing geometry, (iii) a Q-switched, but non injected, frequency doubled Nd:YAG, with a pulse duration of 15 ns in a F/50 focusing geometry. Note that for the two latter test beds, the Rayleigh length is larger than the cell length and no diaphragm is used. Therefore, results from these two test beds and RSG-19 set up can not be directly compared.

3 Results

The results obtained in the F/5 geometry, where the focusing conditions allow to work at high fluences, are reported in figure 1.

Unexpectedly, the optical limiting performances are worse for the combination of nanotubes and modified stilbene-3 than for the nanotubes alone (figure 1, left). In the mixture, limiting is thwarted by an adverse effect. The drop of performances is especially important at low fluences. We also observed that the stability of the composite suspension was poor : aggregation of the nanotubes occurred within a few hours. By contrast, when the suspensions of SWNT and stilbene-3 were prepared in water with the help of surfactants [14], no instability was observed and the optical limiting performances of the mixture

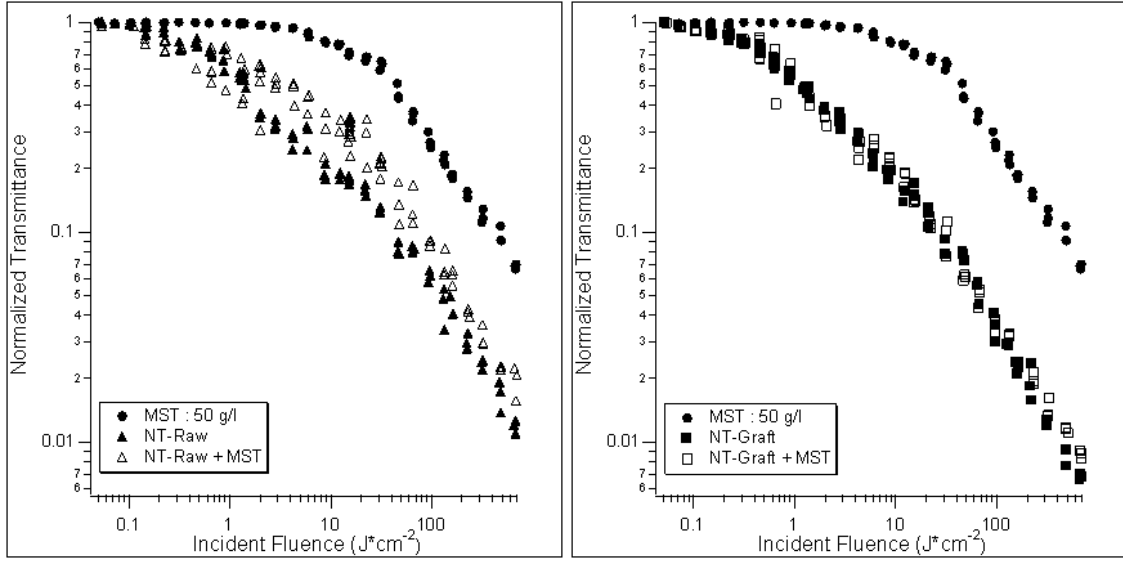


Fig. 1. Optical limiting results at 532 nm, for 7 ns pulses, F/5 geometry and small aperture. The results for the reference samples (SWNT and modified stilbene-3) are compared to those of the mixtures for raw nanotube samples (left) and functionalised nanotubes (right).

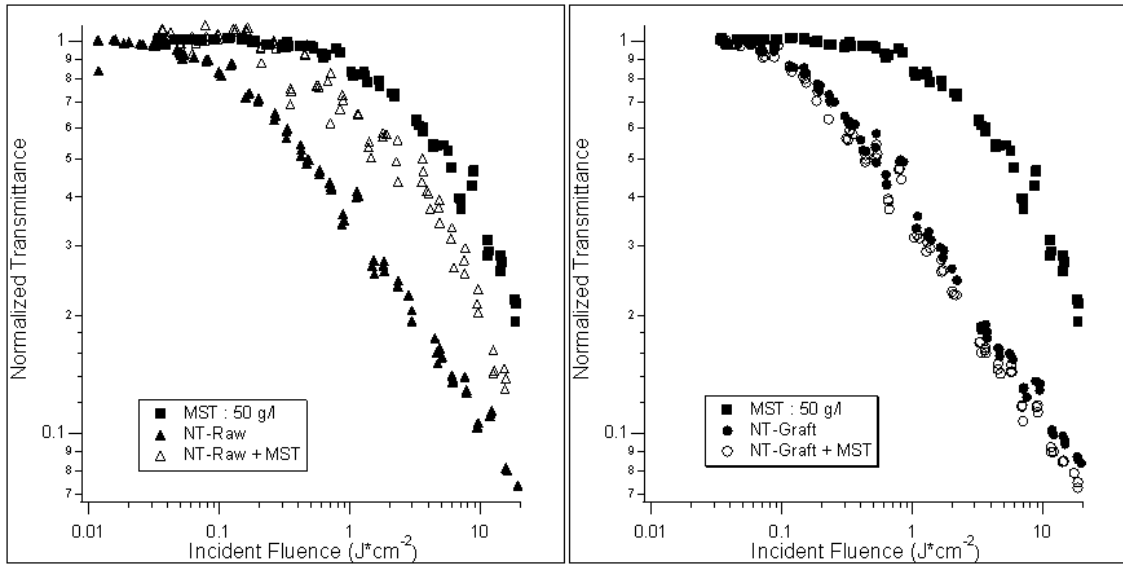


Fig. 2. Optical limiting results at 532 nm, for 15 ns pulses, F/50 geometry. The results for the reference samples are compared to those of the mixtures for raw nanotube samples (left) and functionalised nanotubes (right).

were slightly better than those of the nanotubes alone. On the other hand, if grafted SWNT are used (figure 1, right), the adverse effect disappears although no improvement is observed.

The same samples were studied with a different geometry (F/50) and longer pulses (15 ns). Results are displayed in figure 2. The loss of performances in the

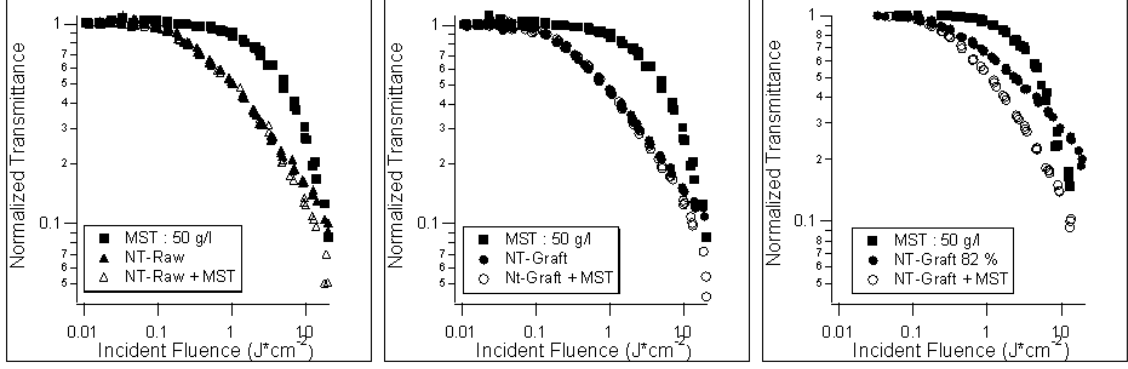


Fig. 3. Optical limiting results at 532 nm, for 3 ns pulses, F/30 geometry. The results for the reference samples are compared to those of the mixtures for raw nanotube samples (left) and for functionalised nanotubes, at regular and low concentrations (70 and 82% transmittance) in the middle and right graphs, respectively.

composite prepared with raw nanotubes is striking (fig. 2, left). The optical limiting threshold is significantly larger than that of the nanotubes alone (200 mJ/cm^{-2} for the mixture vs 50 mJ/cm^{-2} for raw nanotubes). Once again, no adverse effect is observed with composites prepared with functionalised nanotubes. Furthermore, one observes a slight but significant cumulative effect, as initially expected (fig. 2, right).

In the light of these experiments, we assign the adverse effect to an adsorption of the chromophores on the surface of the nanotubes. Such a coating acts as a contact resistance which delays heating of the surrounding solvent. A similar effect has been observed on carbon black suspensions embedded in surfactant [15]. The hypothesis of contact resistance is also confirmed by pump-probe experiments which will be reported elsewhere [16]. Adsorption may be due to π -stacking of the aromatic rings of the MPA over the nanotube surface. In water suspensions, the presence of surfactants prevents the formation of the coating [14]. For functionalised samples, adsorption is hindered by the octadecylamine chains grafted on the nanotube surface which act as steric barriers.

Finally, optical limiting experiments were performed with 3 ns pulses. Results are shown in figure 3. With this set-up, the results are very similar for raw and grafted nanotubes. This is in agreement with the hypothesis of a contact resistance between chromophores and nanotubes. Indeed, for short (3 ns) pulses, nonlinear scattering is mainly due to the sublimation of nanotubes which induces the growth of carbon vapor bubbles [5]. By contrast, for longer (15 ns) pulses, scattering at the limiting threshold is due to the growth of solvent vapor bubbles, nucleated by heat transfert from SWNT to surrounding solvent [5]. While coating of the chromophore on the nanotubes is expected to slow down the heat transfer from SWNT to solvent, one does not expect any change in the heating and sublimation dynamics of the nanotubes.

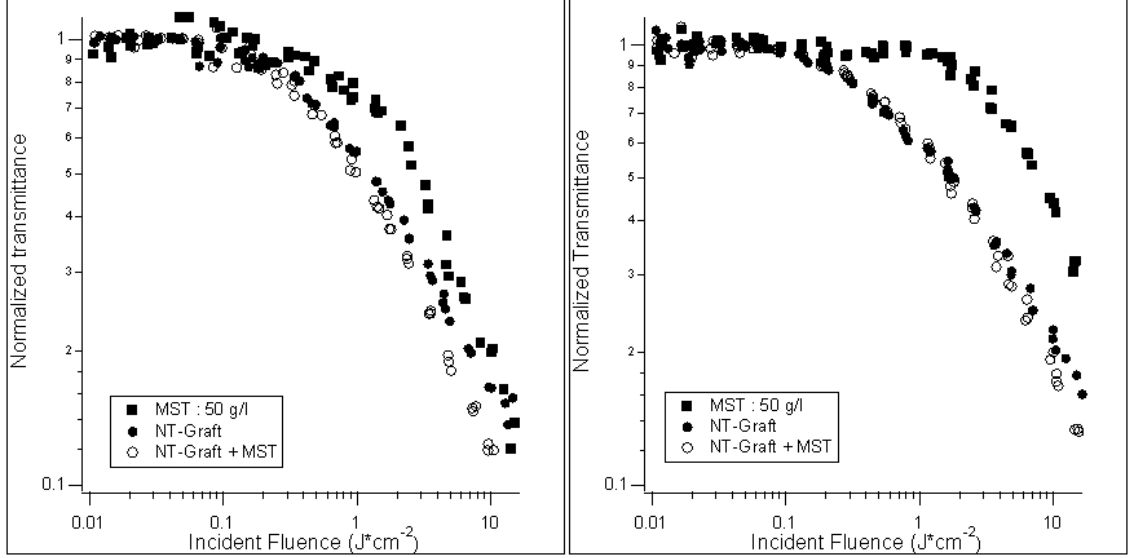


Fig. 4. Optical limiting curves for 3 ns pulses, F/30 geometry at 450 nm (left) and 650 nm (right).

The grafting of long alkyl chains on the nanotubes prevent interactions with the chromophores and allow cumulated efficiencies of both SWNT and MPA. The improvement of the performances due to the cumulative effect is best observed when the limitation efficiency of the chromophores is comparable to that of the nanotubes. This occurs only at high fluences for nanosecond pulses and 70 % transmittance cells. In the right part of figure 3, the cumulative effect is emphasized for a sample prepared with a three times smaller concentration of nanotubes (82 % transmittance). It is obvious that the cumulative effect will also be more effective for larger concentrations of chromophore and/or chromophores with larger multiphoton absorption cross-sections [14]. On the other hand, both non linear scattering from nanotubes and multiphoton absorption are expected to be effective over a broad spectral range. This is confirmed by measurements at various wavelengths, which are displayed in figure 4. The best performances are obtained at small wavelengths, which are associated to nanotubes larger absorbing cross-sections and vapor bubbles larger scattering cross-sections according to Mie theory.

4 Conclusion

The concept of optical limiting systems based on the mixture of carbon nanotubes and multiphoton absorber chromophores was demonstrated. Stable composite suspensions can be prepared, using nanotubes grafted with long alkyl chains. This strategy also inhibits coating of the chromophores on the nanotube surface. We studied the optical limiting properties of the mixtures in

the ns range. When the limiting efficiencies of the two components are close, a cumulative effect is observed. This occurs especially for 3 ns pulses in the case of SWNT/MST mixtures. The range of pulse durations where the cumulative effect will be effective can be easily broadened by increasing the chromophore concentration and/or selecting chromophores with larger multiphoton absorption cross-sections. When the limiting performances of one of the component dominate those of the other, the limiting properties are close to those of the one-component system. This is what we observe for pulses of 7 or 15 ns in the case of SWNT/MST mixtures. Note that optical limiting is effective for suspensions of nanotubes up to microsecond pulses. On the other hand, MPA are good limiters in the sub-nanosecond range. Both nonlinear scattering by nanotubes and non linear absorption by MPA are effective all over the visible range. Therefore, composites SWNT/MPA are promising systems for optical limiting on broad temporal and spectral ranges.

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References

- [1] J.S.Shirk, R.G.S.Pong, S.R.Elom, M.E.Boyle, A.W.Snow, MRS Proceedings 374 (1995) 201-209.
- [2] J.W.Perry, S.Barlow, J.E.Ehrlich, A.A.Heikal, Z.-Y.Hu, I.-Y.S.Lee, K.Mansour, S.R.Marder, H.Röckel, M.Rumi, S.Thayumanavan, X.L.Wu, Nonlinear Optics 21 (1999) 225-243.
- [3] K.J.McEwan, P.K.Milsom, D.B.James, SPIE Proceedings 3472 (1998) 47-52.
- [4] L.Vivien, E.Anglaret, D.Riehl, F.Bacou, C.Journet, C.Goze, M.Andrieux, M.Brunet, F.Lafonta, P.Bernier, F.Hache, Chemical Physics Letters 307 (1999) 317 and erratum, *ibid* 312 (2000) 617.
- [5] L.Vivien, P.Lançon, D.Riehl, F.Hache, E.Anglaret, Carbon 40 (2002) 1789.
- [6] P.A.Miles, Applied Optics 33 (1994) 6965.
- [7] E.W.Van Stryland, S.S.Yang, F.E.Hernandez, V.Dubikovsky, W.Shensky, D.J.Hagan, Nonlinear Optics 27 (2001) 181.
- [8] N.Izard, D.Riehl, E.Anglaret, AIP Conference Proceedings Vol 685, Molecular Nanostructures, (2003) 235-240.
- [9] J.E.Riggs, D.B.Walker, D.L.Caroll, Y.-P.Sun, Journal of Physical Chemistry B 30 (2000) 7071-7076.

- [10] J.Liu, A.G.Rinzler, H.Dai, J.H.Hafner, R.K.Bradley, P.J.Boul, A.Lu, T.Iverson, K.Shelimov, C.B.Huffman, F.Rodriguez-Macias, Y-S.Shon, T.T.Lee, D.T.Colbert, R.E.Smalley, *Science* 280 (1998) 1253.
- [11] J.Chen, M.A.Hamon, H.Hu, Y.Chen, A.M.Rao, P.C.Eklund, R.C.Haddon, *Science* 282 (1998) 95.
- [12] P.-A.Chollet, V.Dumarcher, J.-M. Nunzi, P.Feneyrou, P.Baldek, *Nonlinear Optics* 21 (1999) 299-308.
- [13] D.B.James, K.J.McEwan, *Nonlinear Optics* 21 (1999) 377-389.
- [14] D.Riehl, N.Izard, L.Vivien, E.Anglaret, E.Doris, C.Ménard, C.Mioskowski, L. Porrès, O.Mongin, M.Charlot, M.Blanchard-Desce, R.Anémian, J.-C.Mulatier, C.Barsu, C.Andraud, *Proceedings of SPIE Vol 5211, Nonlinear Optical Transmission and Multiphoton Processes in Organics*, (2003) 124-134.
- [15] F.Fougeanet, D.Riehl, *Nonlinear Optics* 21 (1999) 435-446.
- [16] N.Izard *et al.*, unpublished results.